



## Short communication

# High capacity carbon anode for dry polymer lithium-ion batteries

M. Kawakubo <sup>a,b</sup>, Y. Takeda <sup>b</sup>, O. Yamamoto <sup>b</sup>, N. Imanishi <sup>b,\*</sup>

<sup>a</sup> PRIMIX Corporation, 8-16-43 Ebie, Fukushima, Osaka 553-0001, Japan

<sup>b</sup> Department of Chemistry, Faculty of Engineering, Mie University, 1557 Kurimamachi-cho, Tsu, Mie 514-8507, Japan

## HIGHLIGHTS

- Composite electrodes of MCMB and PEO were prepared using water as a solvent.
- The effect of VGCF and CNTs as conducting additives on the cyclic performance was examined.
- A high reversible capacity of more than 300 mAh g<sup>-1</sup> with an efficiency of 99.4% per cycle was obtained.

## ARTICLE INFO

### Article history:

Received 9 August 2012

Received in revised form

23 September 2012

Accepted 12 October 2012

Available online 23 October 2012

### Keywords:

Carbon anode

Lithium-ion battery

Polymer electrolyte

Polyethylene oxide

## ABSTRACT

A high capacity carbon anode with good cyclability for dry polymer lithium-ion batteries was obtained by the co-addition of vapor grown carbon fiber (VGCF) and carbon nanotubes (CNTs) into a composite carbon electrode of spherical mesocarbon microbeads (MCMB) and a lithium ion conducting binder of polyethylene oxide (PEO) with Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N (LiTFSI). An electrode with MCMB, PEO<sub>19</sub>LiTFSI and VGCF exhibits high reversible capacity of over 330 mAh g<sup>-1</sup>, but poor cycling performance; the capacity retention was 71% at the 50th cycle. In contrast, the electrode with MCMB, PEO<sub>19</sub>LiTFSI, VGCF and CNTs has excellent cycling performance with a reversible capacity of *ca.* 310 mAh g<sup>-1</sup> and reversible capacity retention of 97% at the 50th cycle. The thin and long CNTs could be useful to maintain electrical contact in the cathode matrix during the volume change caused by lithium insertion and extraction into or from the MCMB.

© 2012 Elsevier B.V. All rights reserved.

## 1. Introduction

Large capacity and high energy density batteries have received significant interest in the past decade due to potential applications in electric vehicles (EV) and power stations. Small lithium-ion batteries have been extensively used for cellular phones and laptop computers; however, the safety of larger lithium-ion batteries is still questionable, especially in the case of abusive use. The safety of lithium-ion batteries is mainly related to the thermal reactivity of the components. In order to solve this problem, dry polymer lithium batteries that employ a lithium ion conducting polymer electrolyte have been widely studied [1–4]. Previously developed dry polymer electrolyte lithium batteries have mainly used a lithium metal anode and oxide cathode [1]. Although lithium metal can provide a high energy density, it has safety problems due to dendrite formation on the lithium metal electrode during the charging process [5] and a high reaction heat with the polymer electrolyte of 1.2 J mAh<sup>-1</sup> [6]. Therefore, an

alternative anode for lithium polymer batteries should be developed. The reaction heat of a carbon anode and polymer electrolyte is as low as 0.5 J mAh<sup>-1</sup>, compared to that for a carbon anode and conventional liquid electrolyte of 4.3 J mAh<sup>-1</sup> [7]. However, the carbon anode commonly used for lithium-ion batteries has been recognized to have poor compatibility with polymer electrolytes [6]. Imanishi et al. [6,7] and Kobayashi et al. [8] reported that spherical graphite exhibits a high reversible capacity as the anode for polymer electrolyte batteries, the capacity of which was comparable to that with a liquid electrolyte. However, the capacity of the carbon anode with the polymer electrolyte was dependent on the thickness of the electrode [7]; a high capacity of 310 mAh g<sup>-1</sup> for the *ca.* 30 µm thick electrode was reduced to 150 mAh g<sup>-1</sup> for a *ca.* 100 µm thick electrode. Recently, Imanishi et al. reported that a 60 µm thick composite electrode consisting of spherical mesocarbon microbeads (MCMB), a lithium ion conducting binder of high molecular weight polyethylene oxide (PEO) with Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N (LiTFSI), and vapor grown carbon fiber (VGCF) exhibited good cyclic performance with a high reversible capacity [9]. However, the capacity loss by cycling was *ca.* 0.6% per cycle, which is one order higher than that for practical batteries. A thick electrode is desirable to obtain high specific energy density, because the weight of the

\* Corresponding author. Tel.: +81 59 231 9419; fax: +81 59 231 9478.

E-mail address: [imanishi@chem.mie-u.ac.jp](mailto:imanishi@chem.mie-u.ac.jp) (N. Imanishi).

current collector should be added to the electrode weight; the thickness of the carbon electrode in conventional lithium-ion batteries is in the range of 50–100  $\mu\text{m}$ .

In order to realize a thicker electrode, it is necessary to form a good electric and ionic conduction network in the composite electrode [10]. The electrode for polymer electrolyte batteries should contain the lithium ion conducting polymer electrolyte in the electrode to produce a large reaction area, because the solid electrolyte cannot penetrate into the electrode by self-diffusion as with a liquid electrolyte. Organic solvents such as acetonitrile (AN) have been used for the preparation of composite electrodes with PEO-based lithium conducting polymer electrolytes. The organic solvent is evaporated into the air during the drying process, which pollutes atmosphere and increases the cost of electrode fabrication. Thus, water is a more acceptable and environmentally-friendly solvent for large scale electrode preparation, and its use for electrode preparation has already been proposed [11,12].

In addition, the carbon nanotubes (CNTs) have recently been used as a conductive additive for positive electrodes to improve the capacity retention upon cycling by avoiding contact loss between the active particles [13–15]. Therefore, in this study, composite electrodes of MCMB and PEO were prepared using water as a solvent, and the effect of VGCF and CNTs as conducting additives on the cyclic performance was examined.

## 2. Experimental

MCMB (Osaka Gas Chemicals, Japan, particle size 20–30  $\mu\text{m}$ ,  $c_0 = 0.674 \text{ nm}$ ), VGCF (Showa Denko, Japan, 0.15  $\mu\text{m}$  diameter and 20  $\mu\text{m}$  long, resistivity of single fiber =  $10^{-4} \Omega \text{ cm}$ ,  $c_0 = 0.678 \text{ nm}$ ), water dispersion of CNTs (Shenzhen Multi-Way New Material, China, 10–40 nm diameter and 100  $\mu\text{m}$  long), and PEO (Mw =  $6 \times 10^5$ , Aldrich Chem., USA) were used as starting materials. PEO was dissolved in water and MCMB, VGCF (and/or CNT) were mixed into the solution using a thin-film spin system high-speed mixer (FILMIX Model 40–40 PRIMIX, Japan) at  $5 \text{ m s}^{-1}$  for 30 s. The electrode slurry was spread on a 15  $\mu\text{m}$  thick copper foil using a coating machine and dried at 110  $^\circ\text{C}$  for 10 h under vacuum. For comparison, anhydrous AN was used as a solvent for slurry preparation instead of water. A mixture of MCMB, VGCF, PEO and LiTFSI (Aldrich, USA) (42.1:10.5:34.7:12.7 weight ratio) in AN was stirred overnight in an Ar-filled glove box. The composite electrode was then prepared in the same manner as that with water as the solvent.

The polymer electrolyte of PEO<sub>18</sub>LiTFSI was prepared according to a previously reported method [16]. A given weight of PEO (Mw =  $6 \times 10^5$ ) and LiTFSI (Li/O = 1/18) was dissolved in AN. The solution was stirred overnight and cast in a Teflon dish. After the evaporation of AN at room temperature, the obtained film was dried at 110  $^\circ\text{C}$  for 10 h under vacuum. The thickness of the polymer electrolyte was ca. 300  $\mu\text{m}$ .

The electrode performance was examined using a laminate cell. The cell consisted of the carbon composite electrode, polymer electrolyte, and a lithium metal counter electrode. The active area of the ca. 60  $\mu\text{m}$  thick carbon electrode was 2.25  $\text{cm}^2$ . The test cell was heated at 70  $^\circ\text{C}$  for 1 h to diffuse the LiTFSI salt from the polymer electrolyte to the carbon electrode. The preparation of the polymer electrolyte and construction of the laminate cell were carried out in an Ar-filled glove box. The cells were galvanostatically charged and discharged at 60  $^\circ\text{C}$  in a cut-off voltage range of 0.01–1.5 V using a battery cycler (Nagano BTS 2004H). The charge–discharge rate was C/10 (ca. 0.08  $\text{mA cm}^{-2}$ ). The resistivity of the composite carbon electrodes was examined using the four point probe technique, where the densities of the electrodes were ca. 0.7  $\text{g cm}^{-3}$  (including PEO and conductive additives). Surface images of the electrodes were obtained using scanning electron

microscopy (SEM; Hitachi S-4800). Impedance measurements were performed using a Solartron 1260 frequency analyzer and a Solartron 1286 electrochemical interface in the frequency range of  $10^6$  to 0.1 Hz at 60  $^\circ\text{C}$ .

## 3. Results and discussion

Fig. 1 shows a comparison of the charge and discharge performance of the MCMB–VGCF–PEO (48.2–12.0–39.8 weight ratio) composite carbon electrode prepared using water as a solvent with that of the MCMB–VGCF–PEO<sub>18</sub>LiTFSI (48.2–12.0–39.8 weight ratio) composite carbon electrode prepared using the AN solvent, where the thickness of the composite electrodes was ca. 40  $\mu\text{m}$  and the charge–discharge rate was C/10. The LiTFSI lithium salt is unstable in water; therefore, PEO without LiTFSI in the aqueous starting mixture of the carbon electrode was used. The composite carbon electrode prepared using water has a similar charge–discharge performance and a high reversible capacity of over 300  $\text{mAh g}^{-1}$  to that prepared using the AN solvent. This suggests that LiTFSI is diffused rapidly into the PEO–MCMB–VGCF electrode by contact with PEO<sub>18</sub>LiTFSI at 70  $^\circ\text{C}$ . The lithium salt concentration in the PEO of the composite electrode was estimated to be ca. Li/O = 1/19, assuming the same concentration of LiTFSI in the PEO of both the electrolyte and the composite electrode. Mixing of the electrode components in water using a high speed mixer was quite effective to prepare a homogeneous slurry within a short period of 30 s in open air, which is favorable with respect to both cost and safety concerns [17].

The compositions and resistivities of the carbon electrodes examined in this study are listed in Table 1. The composite electrode of MCMB–VGCF–PEO (48.2–12.0–39.8 weight ratio) (VGCF12) has a considerably low resistivity of 0.47  $\Omega \text{ cm}$  compared to that of

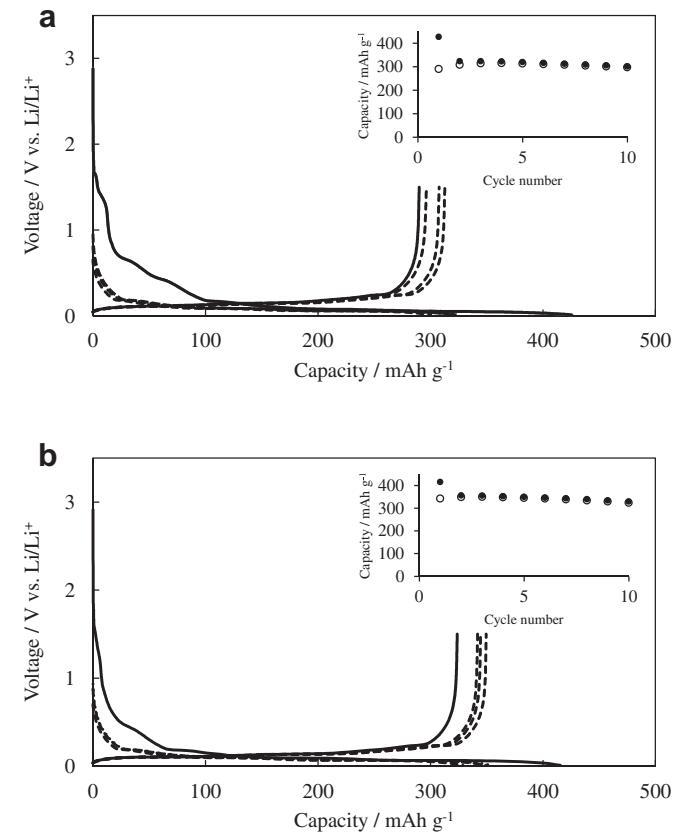


Fig. 1. Charge–discharge curves ( $60^\circ\text{C}$  and C/10 rate,  $0.08 \text{ mA cm}^{-2}$ ) for Li/PEO<sub>18</sub>-LiTFSI/VGCF12 electrodes prepared using (a) AN and (b) water as the solvent. Electrode thickness: ca. 40  $\mu\text{m}$ .

**Table 1**

Composition of electrodes and resistivity at room temperature.

Electrode	Composition (wt.%)				Resistivity (Ω cm)
	MCMB	VGCF	CNT	PEO	
VGCF12	48.2	12.0	—	39.8	0.47
VGCF8/CNT4	48.2	8.0	4.0	39.8	1.61
VGCF6/CNT6	48.2	6.0	6.0	39.8	2.40
CNT12	48.2	—	12.0	39.8	18.66
MCMB	60.2	—	—	39.8	4170

MCMB–PEO (60.2–39.8 weight ratio). The low resistivity of VGCF12 may be due to the low resistivity of the VGCF. The electrical resistivities of pressed samples of MCMB (packing density of  $1.78 \text{ g cm}^{-3}$ ) and VGCF (packing density of  $1.71 \text{ g cm}^{-3}$ ) were  $2.23 \times 10^{-2}$  and  $3.74 \times 10^{-3} \Omega \text{ cm}$ , respectively. The high resistivity of the composite electrode of MCMB–PEO may be due to low contact points between MCMB in the composite, because of a spherical figure of MCMB. The composite electrode of MCMB–CNT–PEO (48.2–12.0–39.8 weight ratio) (CNT12) has a high resistivity of  $18.7 \Omega \text{ cm}$ . The resistivity of CNT was reported to be in a range  $10^{-4}$ – $10^{-5} \Omega \text{ cm}$  [18], which is comparable to that of VGCF. The resistivity is dependent on the conduction path network in the composite electrode; thus, short and thick VGCF may result in a good conduction path with MCMB and PEO, whereas long and thin CNT may not make a good conduction path.

Fig. 2 shows the first three charge–discharge cycles of the Li/PEO<sub>19</sub>LiTFSI/composite electrode cells at 60 °C, where the composite electrode was prepared using water as a solvent and the thickness of that was ca. 60 μm. The charge–discharge rate was C/10. The coulombic efficiencies of the first charge–discharge cycle was 83.4% for VGCF12 (Fig. 2a), 70.1% for VGCF8/CNT4 (Fig. 2b), 63.1% for VGCF6/CNT6 (Fig. 2c), and 55.2% for CNT12 (Fig. 2d). The low coulombic efficiency for CNT12 can be attributed to the large irreversible capacity of the CNTs, as shown in the inset of Fig. 2d. CNTs are considered to be an interesting active material in a liquid electrolyte cell, because Li ions can be inserted in a similar way to that for graphite. However, high irreversible capacity at the first cycle and poor cycling stability were observed [19]. The Li/PEO<sub>19</sub>LiTFSI/CNT cell had a lithium insertion capacity of ca. 600 mAh g<sup>-1</sup> and a lithium extraction capacity of ca. 100 mAh g<sup>-1</sup> at the first cycle. The reversible capacities for the composite electrode with CNT12 increased for the first few cycles. The reversible capacity at the 3rd cycle was in order of VGCF12 > VGCF8/CNT4 > VGCF6/CNT6 > CNT12, which is related to the resistivity of the composite carbon electrodes. Low electrode resistivity results in a good electrical network within the composite carbon electrode, which allows deep lithium insertion into a large part of the MCMB particles. The reversible capacity of VGCF12 at 337 mAh g<sup>-1</sup> is comparable with that of MCMB in EC-DEC-LiClO<sub>4</sub> at 350 mAh g<sup>-1</sup> [7].

The cycling performance of VGCF12, VGCF8/CNT4, VGCF6/CNT6, and CNT12 are shown in Fig. 3. VGCF12 has a high initial capacity of 337 mAh g<sup>-1</sup>; however, the capacity decreases gradually with cycling, and the capacity retention rate after the 50th cycle is 71%. CNT12 shows a capacity increase in the initial few cycles and then gradually decreases; the maximum reversible capacity was only 240 mAh g<sup>-1</sup>. VGCF8/CNT4 exhibited a high reversible capacity of ca. 310 mAh g<sup>-1</sup> and the capacity retention rate was 97% at the 50th cycle. The capacity loss by cycling of VGCF8/CNT4 is approximately one tenth lower than that of VGCF. The cycling stability of VGCF8/CNT4 is comparable to that of MCMB in a conventional liquid electrolyte.

Fig. 4 shows impedance profiles of the Li/PEO<sub>19</sub>LiTFSI/VGCF12 and Li/PEO<sub>19</sub>LiTFSI/CNT12 cells as a function of the electrode potentials (0.01, 0.24, 0.5 and 1.5 V vs. Li/Li<sup>+</sup>) after 10 cycles at 60 °C. The profile for Li/PEO<sub>19</sub>LiTFSI/VGCF12 has three semicircles. The

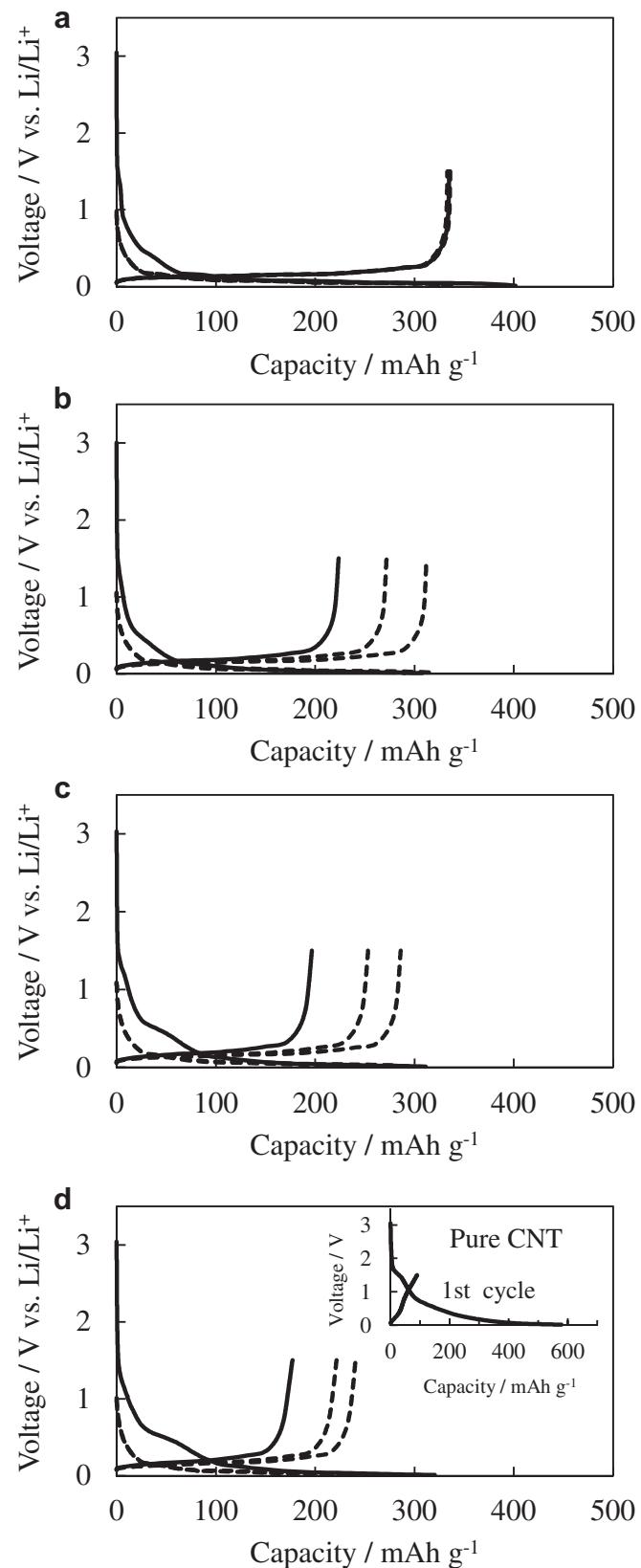
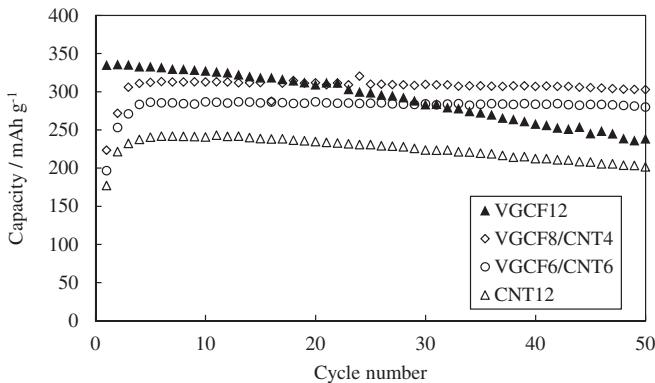
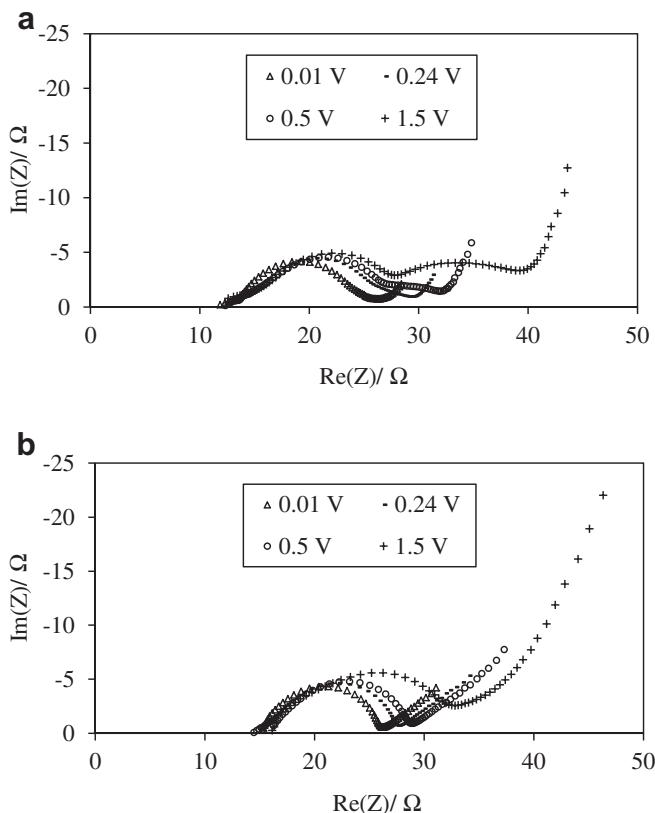


Fig. 2. Charge–discharge curves (60 °C and C/10 rate) for Li/PEO<sub>19</sub>LiTFSI/composite electrodes: (a) VGCF12, (b) VGCF8/CNT4, (c) VGCF6/CNT6, and (d) CNT12. Electrode thickness: ca. 60 μm.



**Fig. 3.** Cycling performance of Li/PEO<sub>19</sub>LiTFSI/composite electrodes at 60 °C: ▲ VGCF12, ◇ VGCF8/CNT4, ○ VGCF6/CNT6, and △ CNT12. Electrode thickness: ca. 60 µm.

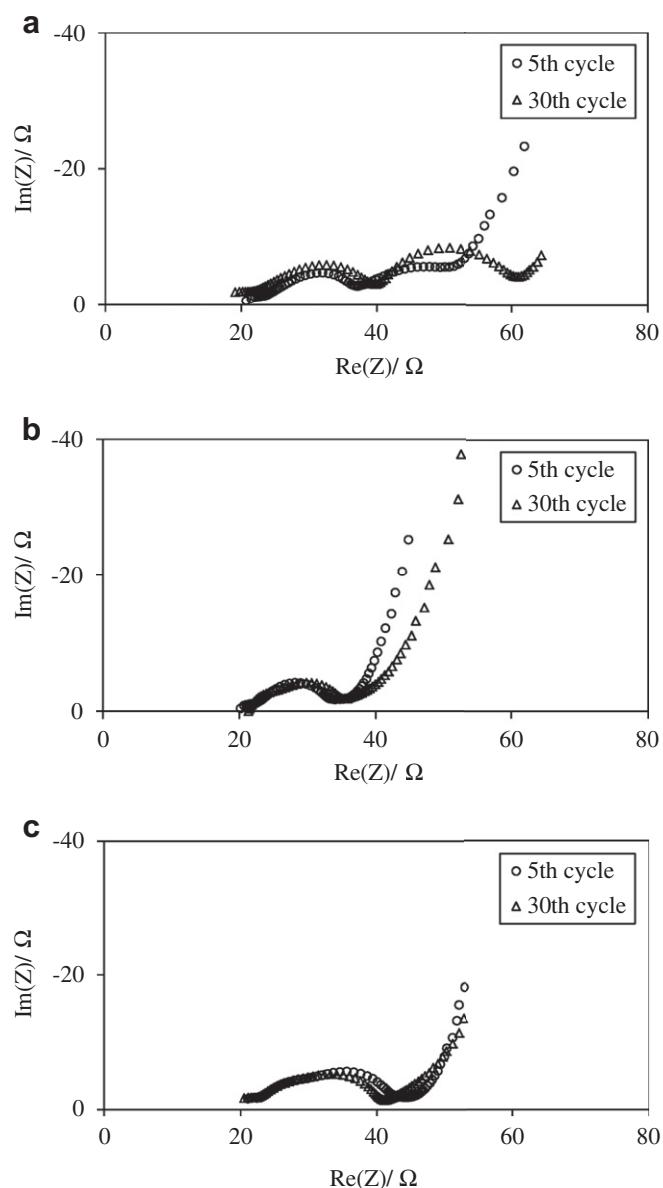
small semicircle at the high frequency range (10<sup>6</sup>–10<sup>5</sup> Hz) may be due to the grain boundary resistance of PEO<sub>19</sub>LiTFSI, because a similar semicircle was observed in the same frequency range for Cu/PEO<sub>18</sub>LiTFSI/Cu. The second semicircle in the medium frequency range (1 × 10<sup>5</sup>–2 × 10<sup>2</sup> Hz) can be attributed to the interfacial resistance between Li metal and the polymer electrolyte ( $R_1$ ), and that at a low frequency range (2 × 10<sup>2</sup>–1 Hz) can be attributed to the interfacial resistance between VGCF12 and the polymer electrolyte ( $R_2$ ). The low frequency semicircle diminished with decrease in the VGCF12 electrode potential, as shown in Fig. 4, which suggests that the low frequency semicircle may correspond to the charge transfer resistance between the polymer electrolyte and the VGCF12 electrode. The charge transfer resistance increased with



**Fig. 4.** Impedance profiles of (a) Li/PEO<sub>19</sub>LiTFSI/VGCF12 and (b) Li/PEO<sub>19</sub>LiTFSI/CNT12 after 10 cycles at 60 °C as a function of the cell potential. Electrode thickness: ca. 60 µm.

decreasing lithium content in MCMB; the charge transfer resistance of 11.8 Ω at 1.5 V decreased to 2.9 Ω at 0.01 V.  $R_1$  showed no significant change with change in the electrode potential of VGCF12. The impedance profiles for Li/PEO<sub>19</sub>LiTFSI/CNT12 at 1.5 V show a small distorted semicircle in the low frequency range of 10<sup>2</sup>–10<sup>1</sup> Hz and no semicircle in the low frequency range at lower potentials. The CNT12 electrode showed a low charge transfer resistance, but it is not sure why CNT prompts the charge transfer reaction of Li + e = Li between PEO<sub>19</sub>LiTFSI and MCMB.

Impedance profiles of the Li/PEO<sub>19</sub>LiTFSI/VGCF12, Li/PEO<sub>19</sub>LiTFSI/CNT12 and Li/PEO<sub>19</sub>LiTFSI/VGCF6/CNT6 cells at 1.5 V vs. Li/Li<sup>+</sup> after 5 and 30 cycles are shown in Fig. 5. There was no significant change in the impedance profiles of the CNT12 and VGCF6/CNT6 electrodes after 5 and 30 cycles, while, the impedance profile of the VGCF12 electrode showed an increase of the semicircle in the low frequency range. The charge transfer resistance of the VGCF electrode (13.4 Ω cm<sup>2</sup>) after 5 cycles increased to 20.7 Ω cm<sup>2</sup> after



**Fig. 5.** Impedance profiles of (a) Li/PEO<sub>19</sub>LiTFSI/VGCF12, (b) Li/PEO<sub>19</sub>LiTFSI/VGCF6/CNT6, and (c) Li/PEO<sub>19</sub>LiTFSI/CNT12 after 5 and 30 cycles at 60 °C. Electrode thickness: ca. 60 µm.

30 cycles. The interface resistance between lithium and  $\text{PEO}_{19}\text{LiTFSI}$  showed no significant change by cycling for all the electrodes. The degradation of capacity by cycling for the VGCF12 could be explained by an increase in the charge transfer resistance between VGCF12 and  $\text{PEO}_{19}\text{LiTFSI}$ . The addition of VGCF into the MCMB and  $\text{PEO}_{19}\text{LiTFSI}$  mixture is effective to reduce the electrode resistance, but the charge transfer resistance is increased with cycling, which may be due to a decrease of the active sites for charge transfer during cycling. On the other hand, the addition of CNTs was not effective to reduce the electrode resistance, but was effective to reduce the charge transfer resistance. Therefore, the addition of both VGCF and CNTs is useful to obtain a high reversible capacity and excellent cycling performance.

Fig. 6 shows SEM images of the VGCF12, CNT12 and VGCF8/CNT4 electrodes. Low resistivity, thick VGCF makes a good conduction network in the PEO and MCMB composite, although the contact between MCMB and PEO may be compromised by expansion and contraction during lithium insertion and extraction into and from MCMB. The long and thin CNTs do not make a good conduction path, but are useful to connect VGCF, PEO and MCMB. CNTs cover the VGCF, PEO, and MCMB matrix like a net, as shown in Fig. 6, and could maintain good contact between MCMB,  $\text{PEO}_{19}\text{LiTFSI}$ , and VGCF to prevent deterioration of the electrode connection network [20]. These SEM images confirm that the co-addition of thick VGCF

with long and thin, high conductivity CNTs with high catalytic activity for the charge transfer reaction, is effective to obtain high reversible capacity for a thick MCMB electrode.

#### 4. Conclusions

Composite carbon electrodes (60  $\mu\text{m}$  thick) were examined for application in dry solid polymer electrolyte batteries. Composite electrodes consisting of PEO, MCMB, VGCF and CNT were prepared in open air using water as a solvent and short-term mixing in a thin-film spin system high-speed mixer. The electrode had the same performance as that for an electrode prepared by conventional mixing with AN as a solvent. Excellent cycling performance with a high reversible capacity of more than 300  $\text{mAh g}^{-1}$  was obtained for MCMB by the co-addition of short and thick VGCF with high conductivity and long and thin CNTs. The reversible capacity loss rate was as low as 0.06% per cycle. The excellent cycling performance can be explained by the formation of a stable conductive network by the co-addition of VGCF and CNTs. VGCF is effective to make a good conductive network and the CNTs assist in the connection of the VGCF, MCMB, and PEO components. A 60  $\mu\text{m}$  thick carbon anode had a reversible capacity per gram of active carbon material comparable to that in a liquid electrolyte; however, the amount of PEO and conductive additive in the carbon electrode was higher than that for a conventional liquid electrolyte. Therefore, the carbon anode should be further improved for application in dry polymer lithium ion batteries, which are considered the best candidate for large lithium-ion batteries with respect to safety.

#### Acknowledgment

This research was sponsored by the Ministry of Education, Culture, Sports, Science & Technology (MEXT) in Japan under the project of the Regional Innovation Strategy Support Program and the Japan Science and Technology Agency (JST) under the Adaptable and Seamless Technology Transfer Program (A-STEP).

#### References

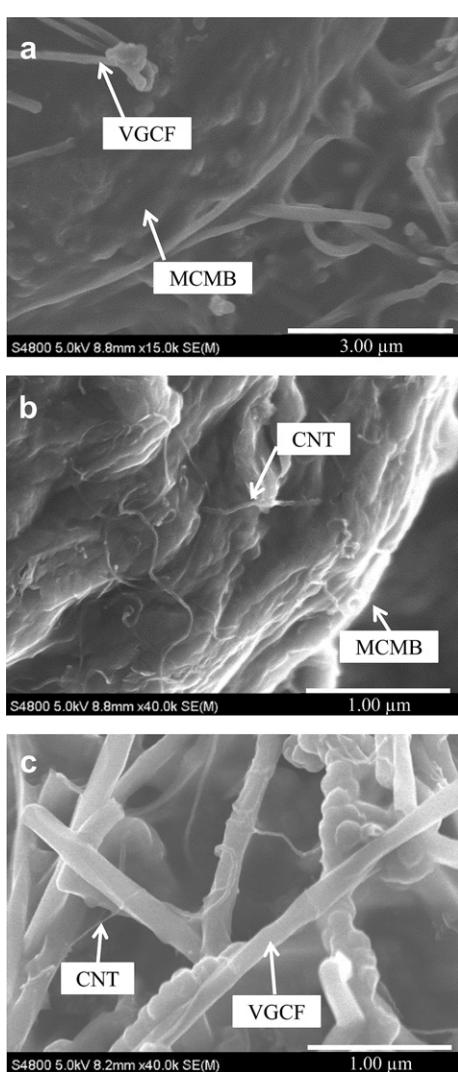


Fig. 6. SEM images of (a) VGCF12, (b) CNT12 and (c) VGCF8/CNT4 electrodes.

- [1] M. Gauthier, D. Fauteux, G. Vassort, A. Bélanger, M. Duval, P. Ricoux, J.M. Chabagno, D. Muller, P. Rigaud, M.B. Armand, D. Deroo, *J. Electrochem. Soc.* 132 (1985) 1333–1340.
- [2] B. Scrosati, F. Croce, S. Panero, *J. Power Sources* 100 (2001) 93–100.
- [3] J.M. Tarascon, M. Armand, *Nature* 414 (2001) 359–367.
- [4] M. Armand, J.M. Tarascon, *Nature* 451 (2008) 652–657.
- [5] C. Brissot, M. Rosso, J.N. Chazalviel, S. Lascaud, *J. Power Sources* 81/82 (1999) 925–929.
- [6] N. Imanishi, Y. Ono, K. Hanai, R. Uchiyama, Y. Liu, A. Hirano, Y. Takeda, O. Yamamoto, *J. Power Sources* 178 (2008) 744–750.
- [7] D. Saito, Y. Ito, K. Hanai, T. Kobayashi, N. Imanishi, A. Hirano, Y. Takeda, O. Yamamoto, *J. Power Sources* 195 (2010) 6172–6176.
- [8] Y. Kobayashi, S. Seki, Y. Mita, Y. Ohno, H. Miyashiro, P. Charest, A. Guerfi, K. Zaghib, *J. Power Sources* 185 (2008) 542–548.
- [9] Y. Ito, M. Kawakubo, M. Ueno, H. Ohkuma, Q. Si, T. Kobayashi, K. Hanai, N. Imanishi, A. Hirano, M.B. Phillipps, Y. Takeda, O. Yamamoto, *J. Power Sources* 214 (2012) 84–90.
- [10] Mohammed H. Al-Saleh, U. Sundararaj, *Carbon* 47 (2009) 2–22.
- [11] J.-H. Lee, S. Lee, U. Paik, Y.-M. Choi, *J. Power Sources* 147 (2005) 249–255.
- [12] S.S. Zhang, K. Xu, T.R. Jow, *J. Power Sources* 138 (2004) 226–231.
- [13] W. Guoping, Z. Qingtang, Y. Zuolong, Q. Meizheng, *Solid State Ionics* 179 (2008) 263–268.
- [14] X. Li, F. Kang, W. Shen, *Electrochim. Solid-State Lett.* 9 (2006) A126–A129.
- [15] L. Kavan, R. Bacsá, M. Tunçkol, P. Serp, S.M. Zakeeruddin, F. Le Formal, M. Zukalova, M. Graetzel, *J. Power Sources* 195 (2010) 5360–5369.
- [16] C. Capiglia, J. Yang, N. Imanishi, A. Hirano, Y. Takeda, O. Yamamoto, *J. Power Sources* 119–121 (2003) 826–832.
- [17] U. Palk, S. Lee, V.A. Hackley, *J. Am. Ceram. Soc.* 86 (2003) 1662–1668.
- [18] T.W. Ebbesen, H.J. Lezec, H. Hiura, J.W. Bennett, H.F. Ghaemi, T. Thio, *Nature* 382 (1996) 54.
- [19] A. Varzi, C. Taibert, M. Wohlfahrt-Mehrens, M. Kreis, W. Schutz, *J. Power Sources* 196 (2011) 3303–3309.
- [20] S.-M. Jang, J. Miyawaki, M. Tsuji, I. Mochida, S.-H. Yoon, F.-Y. Kang, *New Carbon Mater.* 25 (2010) 89–96.